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(54) Title: HEALTHCARE ARTICLE COMPRISING A RANDOM PROPYLENE-ETHYLENE COPOLYMER.

(57) Abstract: The present invention relates to a healthcare article comprising a polymer composition comprising a random propylene-ethylene copolymer, wherein the polymer composition comprises less than 150ppm, preferably less than 100ppm, more preferably less than 50 ppm, more preferably less than 20ppm, most preferably 0 ppm of phthalates based on the weight of the random propylene-ethylene copolymer.



WO 2021/043784 A1

TITLE Healthcare article comprising a random propylene-ethylene copolymer.

TECHNICAL FIELD

The present invention relates to a healthcare article comprising a polymer composition
5 comprising a propylene-ethylene copolymer. The invention further relates to said
polymer composition and use of said polymer composition for the preparation of
healthcare articles.

BACKGROUND

10 Due to increasingly stringent patient safety requirements healthcare professionals are
required to sterilize healthcare articles, such as drug delivery devices. Sterilization is
achieved by exposure of the material to a certain amount of radiation, over a period of
time, e.g. from 1 minute to 24 hours. This treatment however may deteriorate the
properties of the polymer; it can negatively affect the strength, toughness, and
15 aesthetic properties such as colour, taste and odor. Gamma radiation is the most
widely used sterilization method in the healthcare industry. When known random
polypropylene compositions are subjected to the required level of irradiation, e.g. 25-50
kGy gamma radiation or 40kGy electron beam radiation, often a yellowing of the
polymer composition appears, which is undesirable for transparent healthcare articles,
20 such as packaging, as yellowing will make it more difficult for the user to check and
inspect the contents of such packaging.

US 6,664,317 relates to a polyolefin article being essentially phenol antioxidant-free
and having incorporated a stabilizing system sufficient to attenuate the deteriorating
25 effect of gamma radiation, said system consisting of a) one or more hindered amine
stabilizers; b) hydroxylamine and nitron stabilizers; and c) organic phosphites or
phosphonites.

There is therefore, a need for the development of an irradiation resistant, highly
30 transparent, and well processable random polypropylene composition for healthcare
applications, such as drug delivery devices, laboratory ware, medical devices, medical
diagnostics and healthcare packaging.

DRAWINGS

Fig. 1 shows the aTREF spectrum of a phthalate free random propylene-ethylene copolymer (PP-02) and of a phthalate containing random propylene-ethylene copolymer (PP-01).

SUMMARY

It is an object of the present invention to provide a healthcare article showing an improved irradiation resistance, in particular a decreased yellowing, while at the same time having a good transparency and being well processable and which is preferably also suitable for injection molding applications.

This object is achieved by a healthcare article comprising a polymer composition comprising a random propylene-ethylene copolymer, wherein the polymer composition comprises less than 150ppm, preferably less than 100ppm, more preferably less than 50 ppm, more preferably less than 20ppm, most preferably 0 ppm of phthalates based on the weight of the polymer composition.

It has been found that when the healthcare article of the invention is subjected to irradiation it shows less yellowing, while at the same time it maintains its transparency and melt flow rate.

LIST OF DEFINITIONS

The following definitions are used in the present description and claims to define the stated subject matter. Other terms not cited below are meant to have the generally accepted meaning in the field.

“irradiation resistant” as used in the present description means: that the polymer composition shows little to no discolouration (e.g. yellowing) after sterilization via gamma or e-beam irradiation.

In the context of the present invention, “phthalate-free” or “essentially phthalate-free” means having a phthalate content of less than for example 150 ppm, alternatively less than for example 100 ppm, alternatively less than for example 50 ppm, alternatively for example less than 20 ppm, for example having a phthalate content of 0ppm based on

the total weight of the polymer composition, the random propylene-ethylene copolymer or the catalyst composition. The term "phthalates" referring to phthalic acid, its mono- and diesters with aliphatic, alicyclic and aromatic alcohols as well as phthalic anhydride and their respective decomposition products. Phthalates are typically used as internal
5 or external electron donor of Ziegler-Natta catalysts used for polymer production.

Examples of phthalates include but are not limited to a dialkylphthalate esters (having C2-C10 alkyl groups), phthalic acid esters include dimethyl phthalate, diethyl phthalate, ethyl-butyl phthalate, di-n-propyl phthalate, diisopropyl phthalate, di-n-butyl phthalate, diisobutyl phthalate, di-t-butyl phthalate, diisoamyl phthalate, di-t-amyl phthalate,
10 dineopentyl phthalate, di-2-ethylhexyl phthalate, di-2-ethyldecyl phthalate, bis(2,2,2-trifluoroethyl) phthalate, diisobutyl 4-t-butylphthalate, and diisobutyl 4-chlorophthalate and diisodecylphthalate.

"healthcare article" or "article for healthcare application" as used in the present
15 description means:

- surgical instruments;
- drug delivery devices (e.g. injector pens for example for insulin, I.V. bags and sets, and syringes);
- laboratory ware, preferably for biotechnology (e.g. trays, funnels, Petri dishes,
20 filters);
- medical devices, such as blood management devices, e.g. blood filter housing for haemodialysis, kidney dialysis filters, mobile or remote health devices, respiratory devices such as inhalers, medical trays, dental trays, contact lenses;
- medical diagnostics, such as in vitro diagnostics or IVD, monitoring devices,
25 imaging devices; and
- healthcare packaging, such as fluid delivery devices (e.g. bags and tubes), blow-fill-seal packaging, containers and bottles for drugs, e.g. OTC drugs.

DESCRIPTION

30 The melt flow rate (MFR) of the random propylene-ethylene copolymer is for example at least 3.0 dg/min, for example at least 4.0 dg/min, for example at least 5.0 dg/min, for example at least 6.0 dg/min and/or for example at most 100 dg/min, for example at most 95 dg/min, for example at most 90 dg/min.

35 The ethylene content (that is the amount of ethylene monomers incorporated into the random propylene-ethylene copolymer) is for example at least 0.5wt%, for example at

least 1.0wt%, for example at least 1.5wt%, for example at least 2.0wt%, for example at least 2.5wt% and/or for example at most 6.0wt%, for example at most 5.0wt%, for example at most 4.5wt%, for example at most 4.0wt%, for example at most 3.5wt%.

5 The melt flow rate of the random propylene-ethylene copolymer is for example in the range from 3.0 to 100 dg/min, for example the melt flow rate of the random propylene-ethylene copolymer is in the range from 6.0 to 90 dg/min, wherein the melt flow rate (MFR) is determined using ISO1133:2011 (2.16kg, 230°C) and/or wherein the random propylene-ethylene copolymer has an ethylene content as determined using ¹³C NMR in the range from 0.50 to 6.0wt%, preferably in the range from 1.5 to 4.5wt%, more
10 preferably in the range from 2.0 to 4.0wt%, for example in the range from 2.5 to 3.5 wt%.

The total amount of xylene solubles in the random propylene-ethylene copolymer is preferably in the range from 1.0 to 8.0wt% as determined according to ISO16152:2005.

15

For example, the random propylene-ethylene copolymer has a molecular weight distribution (Mw/Mn) of at least 3.0, for example of at least 3.5, for example of at least 4.0 and/or for example of at most 10.0, for example of at most 9.0, for example of at most 8.0, for example of at most 7.5, for example of at most 7.0. For example, the
20 random propylene-ethylene copolymer has a molecular weight distribution (Mw/Mn) in the range from 3.0 to 10.0, for example in the range from 3.5 to 8.0, for example in the range from 4.0 to 7.0, wherein Mw stands for the weight average molecular weight and wherein Mn stands for the number average molecular weight and wherein Mw and Mn are measured by SEC analysis with universal calibration according to ISO16016-
25 1(4):2003.

For example, the random propylene-ethylene copolymer has an area under the aTREF curve at and above a temperature (T) to a temperature up to 120°C of at most 5.0% based on the total area under the aTREF curve in the temperature range from 50°C to

30 120°C, wherein $T = 110 - 1.66*[C]$ equation 1

wherein T is the temperature in °C, wherein [C] is the comonomer content in the random propylene copolymer in wt%

, for example of at most 4.0%, for example of at most 3.0%, for example of at most 2.0%, for example of at most 1.0%, wherein the aTREF curve was generated using a
35 cooling rate of 0.1°C/min and a heating rate of 1°C/min and 1,2-dichlorobenzene as eluting solvent as described herein.

The random propylene-ethylene copolymer is preferably phthalate free, that is it preferably has a phthalate content of less than for example 150 ppm, alternatively less than for example 100 ppm, alternatively less than for example 50 ppm, alternatively for
5 example less than 20 ppm based on the total weight of the random propylene-ethylene copolymer.

Random propylene ethylene copolymers are generally prepared by polymerization of propylene and ethylene in the presence of a catalyst. This type of polymer in the
10 process according to present invention can be produced using any conventional technique known to the skilled person such as bulk polymerization, gas phase polymerization, slurry polymerization, solution polymerization or any combinations thereof. Any conventional catalyst systems, for example, Ziegler-Natta or metallocene may be used. Such techniques, including process conditions, and catalysts are
15 described, for example, in WO06/010414; Polypropylene and other Polyolefins, by Ser van der Ven, Studies in Polymer Science 7, Elsevier 1990; WO06/010414, US4399054 and US4472524. Preferably, the random propylene ethylene copolymer is made using a Ziegler-Natta catalyst.

20 A phthalate free random propylene-ethylene copolymer can be obtained by polymerization of propylene with ethylene by using a phthalate free catalyst system, such as a catalyst system comprising a phthalate free procatalyst (including a phthalate free internal electron donor) as well as a phthalate free external electron. The advantage of such a phthalate free polymer is that it reduces yellowing upon
25 irradiation.

The invention also relates to a process for the preparation of a random propylene-ethylene copolymer, wherein the random propylene-ethylene copolymer is produced from propylene and ethylene in a polymerization process, for example a gas phase
30 polymerization process, in the presence of

- a) a Ziegler-Natta procatalyst comprising compounds of a transition metal of Group 4 to 6 of IUPAC, a Group 2 metal compound and an internal donor, wherein said internal donor is a non-phthalic compound (that is a compound that does not contain phthalates), preferably a non-phthalic acid ester;
- 35 b) a co-catalyst (Co), and
- c) optionally an external donor (ED), preferably a non-phthalic compound.

For example, the procatalyst may be prepared by a process comprising the steps of providing a magnesium-based support, contacting said magnesium-based support with a Ziegler-Natta type catalytic species, an internal donor, and an activator, to yield the
5 procatalyst.

Ziegler-Natta catalyst systems are well known in the art. The term normally refers to catalyst systems comprising a transition metal containing solid catalyst compound (a) and an organo-metal compound (b). Optionally one or more electron donor compounds
10 (external donor) (c) may be added to the catalyst system as well. The transition metal in the transition metal containing solid catalyst compound is normally chosen from groups 4-6 of the Periodic Table of the Elements (Newest IUPAC notation); more preferably, the transition metal is chosen from group 4; the greatest preference is given to titanium (Ti) as transition metal. Although various transition metals are applicable,
15 the following is focused on the most preferred one being titanium. It is, however, equally applicable to the situation where other transition metals than Ti are used. Titanium containing compounds useful in the present invention as transition metal compound generally are supported on hydrocarbon-insoluble, magnesium halides and/or an inorganic oxide, for instance silicon oxide or aluminum oxide, containing
20 supports, generally in combination with an internal electron donor compound. The transition metal containing solid catalyst compounds may be formed for instance by reacting a titanium (IV) halide, an organic internal electron donor compound and a magnesium halide and/or silicon containing support. The transition metal containing solid catalyst compounds may be further treated or modified with an additional electron
25 donor or Lewis acid species and/or may be subjected to one or more washing procedures, as is well known in the art.

In the following paragraphs, examples of different Ziegler-Natta catalysts are given by way of their preparation process.

30

The random propylene-ethylene copolymer may be produced using a Ziegler-Natta catalyst system. Said Ziegler-Natta catalyst system comprising a solid support, preferably a magnesium-based solid support, a transition metal active species, e.g. titanium, and an internal electron donor, preferably a phthalate free internal donor. In
35 case, a phthalate containing internal donor is used, it is clear to the person skilled in the art that the phthalate containing internal donor may be substituted for a non-

phthalic compound, for example by a non-phthalic compound described herein to be suitable as internal electron donor

WO/2015/091982 and WO/2015/091981 describe the preparation of a catalyst system
5 suitable for olefin polymerization, said process comprising the steps of:

- providing a magnesium-based support;
- optionally activating said magnesium-based support;
- contacting said magnesium-based support with a Ziegler-Natta type catalytic species, and optionally one or more internal electron donors to yield a
10 procatalyst, and
- contacting said procatalyst with a co-catalyst and at least one external donor.

Preferably, said procatalyst preparation process comprises the steps of

A) providing said procatalyst obtained via a process comprising the steps of:

15 i) contacting a compound $R^4_zMgX^{4-2z}$ with an alkoxy- or aryloxy-containing silane compound to give a first intermediate reaction product, being a solid $Mg(OR^1)_xX^{1-2-x}$, wherein: R^4 is the same as R^1 being a linear, branched or cyclic hydrocarbyl group independently selected from alkyl, alkenyl, aryl, aralkyl or alkylaryl groups, and one or more combinations thereof; wherein said hydrocarbyl group may be
20 substituted or unsubstituted, may contain one or more heteroatoms and preferably has from 1 to 20 carbon atoms; X^4 and X^1 are each independently selected from the group of consisting of fluoride (F^-), chloride (Cl^-), bromide (Br^-) or iodide (I^-), preferably chloride; z is in a range of larger than 0 and smaller than 2, being $0 < z < 2$;

25 ii) optionally contacting the solid $Mg(OR^1)_xX^{1-2-x}$ obtained in step i) with at least one activating compound to obtain a second intermediate product; wherein: M^1 is a metal selected from the group consisting of Ti, Zr, Hf, Al or Si; M^2 is a metal being Si; v is the valency of M^1 or M^2 ; R^2 and R^3 are each a linear, branched or cyclic hydrocarbyl group independently selected from alkyl, alkenyl, aryl, aralkyl or alkylaryl groups, and one or more combinations thereof; wherein said hydrocarbyl group may be substituted
30 or unsubstituted, may contain one or more heteroatoms, and preferably has from 1 to 20 carbon atoms; and

35 iii) contacting the first or second intermediate reaction product, obtained respectively in step i) or ii), with a halogen-containing Ti-compound, optionally an activator and an internal electron donor to obtain said procatalyst.

WO/2015/091982 and WO/2015/091981 are hereby incorporated by reference. It should be clear to the skilled person that also other external electron donors may be used for preparing a similar catalyst system, for example the external electron donors as exemplified herein. Additional phthalate free Ziegler-Natta catalysts, which may
5 suitably be used to prepared the random propylene-ethylene copolymer of the invention are described in WO2015/091983, hereby incorporated by reference.

EP 1 273 595 of Borealis Technology discloses a process for producing an olefin polymerization procatalyst in the form of particles having a predetermined size range,
10 said process comprising: preparing a solution a complex of a Group IIa metal and an electron donor by reacting a compound of said metal with said electron donor or a precursor thereof in an organic liquid reaction medium; reacting said complex, in solution, with at least one compound of a transition metal to produce an emulsion the dispersed phase of which contains more than 50 mol.% of the Group IIa metal in said
15 complex; maintaining the particles of said dispersed phase within the average size range 10 to 200 μm by agitation in the presence of an emulsion stabilizer and solidifying said particles; and recovering, washing and drying said particles to obtain said procatalyst. EP 1275595 and in particular the above described production method, is hereby incorporated by reference.

20

EP 0 019 330 of Dow discloses a Ziegler-Natta type catalyst composition. Said olefin polymerization catalyst composition is prepared using a process comprising: a) a reaction product of an organo aluminum compound and an electron donor, and b) a solid component which has been obtained by halogenating a magnesium compound
25 with the formula MgR^1R^2 wherein R^1 is an alkyl, aryl, alkoxide or aryloxy group and R^2 is an alkyl, aryl, alkoxide or aryloxy group or halogen, are contacted with a halide of tetravalent titanium in the presence of a halohydrocarbon, and contacting the halogenated product with a tetravalent titanium compound. This production method as disclosed in EP 0 019 330 is incorporated by reference.

30 Example 2 of US 6,825,146 of Dow discloses another improved process to prepare a catalyst. Said process includes a reaction between titanium tetrachloride in solution with a precursor composition - prepared by reacting magnesium diethoxide, titanium tetraethoxide, and titanium tetrachloride, in a mixture of ortho-cresol, ethanol and chlorobenzene - and ethylbenzoate as electron donor. The mixture was heated and a
35 solid was recovered. To the solid titanium tetrachloride, a solvent and benzoylchloride were added. The mixture was heated to obtain a solid product. The last step was

repeated. The resulting solid procatalyst was worked up to provide a catalyst. Example 2 of US 6,825,146 is incorporated by reference.

5 US 4,771,024 discloses the preparation of a catalyst on column 10, line 61 to column 11, line 9. The section "catalyst manufacture on silica" is incorporated into the present application by reference. The process comprises combining dried silica with carbonated magnesium solution (magnesium diethoxide in ethanol was bubbled with CO₂). The solvent was evaporated at 85 °C. The resulting solid was washed and a 50:50 mixture of titanium tetrachloride and chlorobenzene was added to the solvent
10 together with ethylbenzoate. The mixture was heated to 100 °C and liquid filtered. Again TiCl₄ and chlorobenzene were added, followed by heating and filtration. A final addition of TiCl₄ and chlorobenzene and benzoylchloride was carried out, followed by heating and filtration. After washing the catalyst was obtained.

15 US 4,866,022 discloses a catalyst component comprises a product formed by: A. forming a solution of a magnesium-containing species from a magnesium carbonate or a magnesium carboxylate; B. precipitating solid particles from such magnesium-containing solution by treatment with a transition metal halide and an organosilane having a formula: R_nSiR'_{4-n}, wherein n= 0 to 4 and wherein R is hydrogen or an alkyl, a haloalkyl or aryl radical containing one to about ten carbon atoms or a halosilyl
20 radical or haloalkylsilyl radical containing one to about eight carbon atoms, and R' is OR or a halogen; C. reprecipitating such solid particles from a mixture containing a cyclic ether; and D. treating the reprecipitated particles with a transition metal compound and an electron donor. This process for preparing a catalyst is incorporated
25 into the present application by reference. In a preferred embodiment, the catalyst preparation process comprises the steps of reacting a magnesium-containing species, a transition metal halide and an organosilane, again with transition metal compound and an electron donor.

30 The Ziegler-Natta type procatalyst may for example also be that of the catalyst system that is obtained by the process as described in WO 2007/134851 A1. In Example I the process is disclosed in more detail. Example I including all sub-examples (IA-IE) of WO 2007/134851 A1 is incorporated into the present description. More details about the different embodiments are disclosed starting on page 3, line 29 to page 14 line 29 of
35 WO 2007/134851 A1. These embodiments are incorporated by reference into the present description.

The catalyst used for preparation of the random propylene-ethylene copolymer may for example also be the catalyst system that is obtained by the process as described in EP3212712B1, for example the process as described in paragraphs [0159] – [0162],
5 EP3212712B1 and in particular paragraphs [0159] – [0162] of EP3212712B1 are hereby incorporated by reference.

In case an internal electron donor compound (also referred to herein as “internal electron donor”, or “internal donor”) is used in the catalysts used for the preparation of
10 the random propylene-ethylene copolymer, in order to achieve a phthalate-free random propylene-ethylene copolymer, the internal electron donor is preferably phthalate free, that is the internal donor is a non-phthalic compound (a compound that does not contain phthalates), preferably a non-phthalic acid ester;

15 The non-phthalic internal donor is preferably selected from (di)esters of non-phthalic carboxylic (di)acids, non-phthalic (aromatic) acid esters, 1,3-diethers, derivatives, aminobenzoates and mixtures thereof.

Examples of diester of non-phthalic carboxylic di acids include esters belonging to a
20 group consisting of malonates, maleates, succinates, citraconates, for example bis(2-ethylhexyl)citraconate, glutarates, cyclohexene-1,2-dicarboxylates and benzoates, silyl esters, and any derivatives and/or mixtures thereof.

Suitable non-limiting examples of phthalate free aromatic acid esters, for example
25 benzoic acid esters include an alkyl p-alkoxybenzoate (such as ethyl p-methoxybenzoate, methyl p-ethoxybenzoate, ethyl p-ethoxybenzoate), an alkyl benzoate (such as ethyl benzoate, methyl benzoate), an alkyl p-halobenzoate (ethyl p-chlorobenzoate, ethyl p-bromobenzoate), and benzoic anhydride. The benzoic acid ester is preferably selected from ethyl benzoate, benzoyl chloride, ethyl p-
30 bromobenzoate, n-propyl benzoate and benzoic anhydride. The benzoic acid ester is more preferably ethyl benzoate.

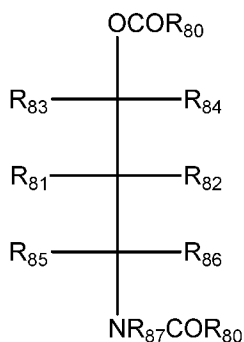
Suitable examples of phthalate free 1,3- diethers compounds include but are not limited to diethyl ether, dibutyl ether, diisoamyl ether, anisole and ethylphenyl ether, 2,3-
35 dimethoxypropane, 2,3-dimethoxypropane, 2-ethyl-2-butyl-1,3-dimethoxypropane, 2-isopropyl-2-isopentyl- 1,3-dimethoxypropane and 9,9-bis (methoxymethyl) fluorene.

Suitable examples of phthalate free succinates, for example succinate acid esters include but are not limited to diethyl 2,3-di-isopropylsuccinate, diethyl 2,3-di-n-propylsuccinate, diethyl 2,3-di-isobutylsuccinate, diethyl 2,3-di-sec-butylsuccinate,
 5 dimethyl 2,3-di-isopropylsuccinate, dimethyl 2,3-di-n-propylsuccinate, dimethyl 2,3-di-isobutylsuccinate and dimethyl 2,3-di-sec-butylsuccinate.

The phthalate free silyl ester as internal donor can be any silyl ester or silyl diol ester known in the art, for instance as disclosed in US 2010/0130709.

10

Phthalate free aminobenzoates as internal donors may be represented by formula (XI):



Formula XI

wherein:

15 R^{80} , R^{81} , R^{82} , R^{83} , R^{84} , R^{85} , R^{86} and R^{87} are independently selected from a group consisting of hydrogen or C₁-C₁₀ hydrocarbyl.

For example, the internal electron donor is selected from the group consisting of 4-[benzoyl(methyl)amino]pentan-2-yl benzoate; 2,2,6,6-tetramethyl-

20 5-(methylamino)heptan-3-ol dibenzoate; 4-[benzoyl (ethyl)amino]pentan-2-yl benzoate, 4- (methylamino)pentan-2-yl bis (4-methoxy)benzoate); 3-[benzoyl(cyclohexyl)amino]-1-phenylbutylbenzoate; 3-[benzoyl(propan-2-yl)amino]-1-phenylbutyl; 4-[benzoyl(methyl)amino]-1,1,1-trifluoropentan-2-yl; 3-(methylamino)-1,3-diphenylpropan-1-ol dibenzoate; 3-(methyl)amino-propan-1-ol dibenzoate; 3-
 25 (methyl)amino-2,2-dimethylpropan-1-ol dibenzoate, and 4-(methylamino)pentan-2-yl-bis (4-methoxy)benzoate).

The molar ratio of the internal donor relative to the magnesium can be from 0.020 to 0.50. Preferably, this molar ratio is from 0.050 to 0.20.

30

As discussed in WO 2013/124063, hereby incorporated by reference, 1,5-diesters, for example pentanediol dibenzoate, preferably meso pentane-2,4-diol dibenzoate (mPDDB), can be used as internal donors.

As used herein, a "co-catalyst" is a term well-known in the art in the field of Ziegler-Natta catalysts and is recognized to be a substance capable of converting the
5 procatalyst to an active polymerization catalyst. Generally, the co-catalyst is an organometallic compound containing a metal from group 1, 2, 12 or 13 of the Periodic System of the Elements (Handbook of Chemistry and Physics, 70th Edition, CRC Press, 1989- 1990). The co-catalyst may include any compounds known in the art to be
10 used as "co-catalysts", such as hydrides, alkyls, or aryls of aluminum, lithium, zinc, tin, cadmium, beryllium, magnesium, and combinations thereof. The co-catalyst may be a hydrocarbyl aluminum co-catalyst as are known to the skilled person. Preferably, the cocatalyst is selected from trimethylaluminum, triethylaluminum, triisobutylaluminum, trihexylaluminum, di-isobutylaluminum hydride, trioctylaluminum, dihexylaluminum
15 hydride and mixtures thereof, most preferably, the cocatalyst is triethylaluminum (abbreviated as TEAL).

In case an optional external electron donor compound (also referred to herein as "external electron donor", or "external donor") is used in the catalysts used for the
20 preparation of the random propylene-ethylene copolymer, in order to achieve a phthalate-free random propylene-ethylene copolymer, the external electron donor is preferably phthalate free, that is a non-phthalic compound.

Examples of external donors are known to the person skilled in the art and include but
25 are not limited to external electron donors chosen from the group of a compound having a structure according to Formula III $(R^{90})_2N-Si(OR^{91})_3$, a compound having a structure according to Formula IV: $(R^{92})Si(OR^{93})_3$ and mixtures thereof wherein each of R^{90} , R^{91} , R^{92} and R^{93} groups are each independently a linear, branched or cyclic, substituted or unsubstituted alkyl having from 1 to 10 carbon atoms,
30 preferably wherein R^{90} , R^{91} , R^{92} and R^{93} groups are each independently a linear unsubstituted alkyl having from 1 to 8 carbon atoms, for example ethyl, methyl or n-propyl, for example diethylaminotriethoxysilane (DEATES), n-propyl triethoxysilane, (nPTES), n-propyl trimethoxysilane (nPTMS); and organosilicon compounds having general formula $Si(OR^a)_{4-n}R^b_n$, wherein n can be from 0 up to 2, and each of R^a and R^b ,
35 independently, represents an alkyl or aryl group, optionally containing one or more hetero atoms for instance O, N, S or P, with, for instance, 1-20 carbon atoms; such as

diisobutyl dimethoxysilane (DiBDMS), t-butyl isopropyl dimethoxysilane (tBuPDMS), cyclohexyl methyl dimethoxysilane (CHMDMS), dicyclopentyl dimethoxysilane (DCPDMS) or di(iso-propyl) dimethoxysilane (DiPDMS). More preferably, the external electron donor is chosen from the group of di(iso-propyl) dimethoxysilane (DiPDMS) or
 5 diisobutyl dimethoxysilane (DiBDMS).

The molar ratio of the co-catalyst to the procatalyst (Al/Ti) in the catalyst polymerization system may for example be from about 5:1 to about 500:1 or from about 10:1 to about 200:1 or from about 15:1 to about 150:1 or from about 20:1 to about 100:1.

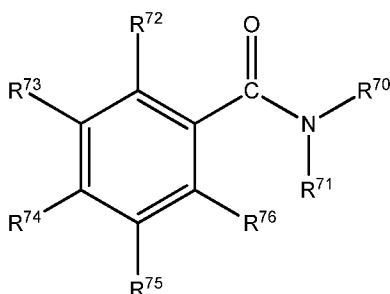
10

The molar ratio of the external donor to the pro-catalyst (Si/Ti) in the catalyst polymerization system, may for example be in the range from 1 to 100, for example in the range from 20-80.

15 The molar ratio of the co-catalyst to the external donor (Al/Si) in the catalyst polymerization system may for example be from preferably is from 0.1 to 200; more preferably from 1 to 100, for example from 5 to 50.

The catalyst system comprising the Ziegler-Natta pro-catalyst may be activated with an
 20 activator, for example an activator chosen from the group of benzamides and monoesters, such as alkylbenzoates.

For example, the activator may be a benzamide according to formula X:

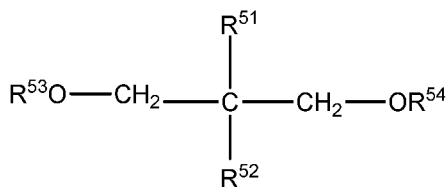


Formula X

25 wherein R^{70} and R^{71} are each independently selected from hydrogen or an alkyl, and R^{72} , R^{73} , R^{74} , R^{75} , R^{76} are each independently selected from hydrogen, a heteroatom or a hydrocarbonyl group, preferably selected from alkyl, alkenyl, aryl, aralkyl, alkoxy carbonyl or alkylaryl groups, and one or more combinations thereof;

Examples of such activators include but are not limited to N,N,-dimethylbenzamide, methylbenzoate, ethylbenzoate, ethyl acetate, and butyl acetate, more preferably the activator is ethylbenzoate or benzamide.

- 5 In a preferred embodiment a catalyst system comprising a Ziegler-Natta catalyst that has been activated with an activator, further comprises as internal donor an internal donor chosen from the group of phthalate-free internal donors, for example chosen from the group of 1,3-diethers, such as represented by the Formula VII,



- 10 Formula VII

wherein R⁵¹ and R⁵² are each independently selected from a hydrogen or a hydrocarbyl group selected from alkyl, alkenyl, aryl, aralkyl, alkoxy carbonyl or alkylaryl groups, and one or more combinations thereof and wherein R⁵³ and R⁵⁴ are each independently selected from a hydrocarbyl group, preferably selected from alkyl, alkenyl, aryl, aralkyl, alkoxy carbonyl or alkylaryl groups, and one or more combinations thereof; preferably 15 9,9-bis (methoxymethyl) fluorene.

- For example, the random propylene-ethylene copolymer is present in the polymer composition in an amount of at least 80wt% based on the weight of the polymer composition, for example at least 85wt% based on the weight of the polymer composition, for example at least 90wt% based on the weight of the polymer composition, for example at least 95wt% based on the weight of the polymer composition, preferably at least 97wt% based on the weight of the polymer composition, preferably at least 98wt% based on the weight of the polymer composition, more 20 preferably in an amount of at least 99wt% based on the weight of the polymer composition. The remaining percentage up to 100 wt.% preferably being formed of one or more additives, such as the stabilizing additive mixture described below.

- Preferably, the polymer composition of the invention further comprises a stabilizing additive mixture, said stabilizing additive mixture comprising a hydroxylamine, a phosphite compound and a hindered amine light stabilizer. Such polymer composition shows a further decrease in yellowing after irradiation. It is resistant to irradiation by the fact that it does not show (significant) yellowing after irradiation with e.g. gamma 30

radiation (e.g. 35-55 kGy) or electron beam radiation (e.g. 40 kGy). It shows high transparency and has a high melt flow rate. The present invention allows for maximum patient safety and adherence (transparency and non-yellowing) and enhanced processing behaviour (high MFR) leading to reduces costs.

5 The amount of stabilizing additive mixture is for example at least 0.040wt%, for example at least 0.10wt%, for example at least 0.12 wt% and/or for example at most 0.60wt%, for example at most 0.50wt%, for example at most 0.60 wt% based on the weight of the polymer composition.

10 For example, said stabilizing additive mixture is present in an amount of from 0.040 to 0.60 wt.% based on the weight of the polymer composition, preferably from 0.12 to 0.40.

For example, the polymer composition comprises only one type of polymer, being a
15 random propylene-ethylene copolymer. In said embodiment, the polymer composition consists of the random propylene-ethylene copolymer and additives, such as a stabilizing additive mixture.

For example, the hydroxylamine is N,N-dioctadecylhydroxylamine. For example, N,N-
20 dioctadecylhydroxylamine Irgastab® FS-042 of BASF having a CAS number of 143925-92-2 may be used. The hydroxylamine may for example be present in an amount from at least 0.010, for example from at least 0.020, for example from at least 0.030 and/or in an amount of at most 0.15, for example in an amount of at most 0.10wt% based on the weight of the polymer composition. For example, the hydroxylamine is present in an
25 amount from 0.01 to 0.15 wt.% based on the weight of the polymer composition, preferably in an amount from 0.03 to 0.10 wt.% based on the weight of the polymer composition.

For example the phosphite compound is tris(2,4-di-tert-butylphenyl)phosphite. For
30 example, tris(2,4-di-tert-butylphenyl)phosphite, Irgafos® 168 of BASF, , having a CAS number of 31570-04-4, may be used. For example, the phosphite is present in an amount from at least 0.010, for example from at least 0.020, for example from at least 0.030 and/or to at most 0.15, for example to at most 0.10wt% based on the weight of the polymer composition.

For example, the phosphite is present in an amount from 0.010 to 0.15 wt.% based on the weight of the polymer composition, preferably in an amount from 0.030 to 0.10 wt.% based on the weight of the polymer composition.

- 5 For example, the hindered amine light stabilizer is butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol. The hindered amine light stabilizer is for example present in an amount from at least 0.020, for example from an amount of at least 0.030, for example at least 0.040, for example at least 0.050, for example at least 0.060 and/or at most 0.30, for example at most 0.25, for
10 example at most 0.20wt% based on the polymer composition. For example, the the hindered amine light stabilizer is present in an amount from 0.020 to 0.30 wt.% based on the weight of the polymer composition, preferably in an amount from 0.060 to 0.20 wt.% based on the weight of the polymer composition.
- 15 For example, the hindered amine light stabilizer may be poly(4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol-*alt*-1,4-butanedioic acid (also called butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol). For example, as butanedioic acid, dimethylester polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol Tinuvin® 622 of BASF may be used, having a CAS
20 number of CAS 65447-77-0.

The polymer composition may further comprise a clarifier additive to enhance transparency. For example as a clarifier additive, 1,2,3-tridesoxy-4,6;5,7-bis-O-[(4-propylphenyl) methylene] nonitol sorbitol may be used. For example, 1,2,3-tridesoxy-
25 4,6;5,7-bis-O-[(4-propylphenyl) methylene] nonitol sorbitol Millad® NX8000 from Milliken may be used.

For example, the clarifier additive may be present in an amount of at least 0.10, for example of at least 0.15, for example of at least 0.20 and/or of at most 0.40, for
30 example at most 0.30, for example at most 0.35wt% based on the weight of the polymer composition.

For example, the clarifier additive may be present in an amount from 0.10 to 0.40wt%, more preferably from 0.20 to 0.30wt% based on the weight of the polymer composition

- 35 The polymer composition may further comprise an antistatic additive, preferably a glycerol ester, more preferably a mono-ester of a C16-C24 alkyl acid – e.g. stearic

acid, with glycerol. Most preferably, as antistatic additive Atmer® 129 of Croda (CAS 31566-31-1) is used. The antistatic additive may be present in an amount from 0.020 to 0.20 wt.%, preferably from 0.080 to 0.12 wt.% based on the weight of the polymer composition.

5 For example, a mixture of hydroxylamine and phosphite compound, preferably a 1:1 mixture, is used to prepare the polymer composition. Preferably, a 1:1 mixture of N,N-dioctadecylhydroxylamine and tris(2,4-di-tert-butylphenyl)phosphite is used, being Irgastab FS 301 of BASF.

10 In a specific embodiment, said stabilizing additive mixture comprises N,N-dioctadecylhydroxylamine, tris(2,4-di-tert-butylphenyl)phosphite, and butanedioic acid, dimethylester polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol.

In a specific embodiment, the stabilizing additive mixture comprises from 0.010 to 0.15
15 wt.% N,N-dioctadecylhydroxylamine, from 0.010 to 0.15 wt.% tris(2,4-di-tert-butylphenyl)phosphite, and from 0.020 to 0.30 wt.% butanedioic acid, dimethylester polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol, each based on the weight of the polymer composition.

20 In a specific embodiment, the stabilizing additive mixture comprises from 0.030 to 0.10 wt.% N,N-dioctadecylhydroxylamine, from 0.030 to 0.10 wt.% tris(2,4-di-tert-butylphenyl)phosphite, and from 0.060 to 0.20 wt.% butanedioic acid, dimethylester polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol, each based on the weight of the polymer composition.

25

In a specific embodiment, the stabilizing additive mixture comprises from 0.040 to 0.060 wt.% N,N-dioctadecylhydroxylamine, from 0.040 to 0.060 wt.% tris(2,4-di-tert-butylphenyl)phosphite, and from 0.080 to 0.12 wt.% butanedioic acid, dimethylester
30 polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol, each based on the weight of the polymer composition.

The polymer composition may further comprise an acid scavenger, preferably calcium (Ca) stearate. For example, the polymer composition may comprise the acid scavenger in an amount from 0.025 to 0.15 wt.%, such as from 0.050 to 0.10 wt. % of the acid
35 scavenger, based on the weight of said polymer composition.

The polymer composition may further comprise a UV stabilizer, preferably poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidiny)imino]-1,6 hexanediy][(2,2,6,6-tetramethyl-4-piperidiny)imino]] (Chimasorb 944FD or Sabostab UV94 / = HALS)

5

Preferably, the polymer composition is free of phenolic additives, that is preferably the polymer composition has less than 10 ppm of phenolic additives.

Preferably, the article according to the invention has a CIELAB b-value, as determined according to ASTM D6290-05 and ASTM E313 of at most 4.0, preferably of at most 3.0, more preferably of at most 2.5, even more preferably of at most 2.0 after having being subjected to at least 25 kGy gamma radiation, preferably after having been subjected to at least 50 kGy gamma radiation or at least 40 kGy electron beam radiation.

15 In another aspect, the invention relates to a polymer composition comprising a random propylene-ethylene copolymer and a stabilizing additive mixture, said stabilizing additive mixture comprising a hydroxylamine, a phosphite compound and a hindered amine light stabilizer, and optionally a clarifier additive, preferably wherein the polymer composition comprises less than 150ppm, preferably less than 100ppm, more preferably less than 50 ppm, more preferably less than 20ppm, most preferably 0 ppm of phthalates based on the weight of the random propylene ethylene copolymer.

In another aspect, the invention relates to the use of the polymer composition as identified herein for manufacturing a healthcare article, for example wherein the healthcare article is a drug delivery article, laboratory ware, a medical device, a medical diagnostics article or healthcare packaging.

The healthcare article of the invention may be prepared from the polymer composition using techniques known per se. For example the healthcare article may be prepared by extrusion of injection moulding, preferably injection moulding. Injection moulding is a technique that is widely used to prepare for example (rigid) packaging and durables.

In another aspect, the invention relates to a process for the preparation of a healthcare article comprising the steps of

35 providing a polymer composition as described herein

Injection moulding of the polymer composition to provide the healthcare article.

In another aspect, the invention relates to the use of the polymer composition as described herein for manufacturing a healthcare article with reduced yellowing after irradiation, for example with reduced yellowing after irradiation with 25 kGy gamma
5 radiation.

The invention further relates to a use of the polymer composition for manufacturing a healthcare article with increased resistance for irradiation. The invention further relates to a use of the polymer composition according to the invention for manufacturing a
10 healthcare article having a CIELAB b-value, as determined according to ASTM D6290-05 and ASTM E313 of at most 4.0, preferably of at most 3.0, more preferably of at most 2.5, even more preferably of at most 2.0 after having being subjected to at least 25 kGy gamma radiation, preferably after having been subjected to at least 50 kGy gamma radiation or at least 40 kGy electron beam radiation.

15 The invention also relates to a process for preparing an irradiated healthcare article, comprising the steps of providing a polymer composition and extruding or injection moulding of said polymer composition to provide the healthcare article and irradiating the healthcare article with gamma radiation or electron beam radiation.

20 In another aspect, the invention relates to an irradiated healthcare article obtained or obtainable by said process.

All variations discussed above for the article are also applicable to the uses, the
25 polymer compositions and to the processes. Other variations to the disclosed embodiments can be understood and effected by those skilled in the art in practicing the claimed invention, from a study of the drawings, the disclosure, and the appended claims. In the claims, the word "comprising" does not exclude other elements or steps, and the indefinite article "a" or "an" does not exclude a plurality. The scope of the
30 present invention is defined by the appended claims. One or more of the objects of the invention are achieved by the appended claims.

The invention will now be elucidated by way of the following examples, without however, being limited thereto.

35

Examples

Measurement methodsMelt flow rate (MFR)

The melt flow rate (MFR) was determined according to ISO1133-1:2011, 230°C,
5 2.16kg.

Cold xylene solubles (XS)

The XS was determined in the following way: 1 gram of polymer and 100 ml of xylene were introduced in a glass flask equipped with a magnetic stirrer. The temperature was raised up to the boiling point of the solvent. The so obtained clear solution was then
10 kept under reflux and stirring for further 15 minutes. Heating was stopped and the isolating plate between heating and flask was removed. Cooling took place with stirring for 5 minutes. The closed flask was then kept for 30 minutes in a thermostatic water bath at 25°C for 30 minutes. The so formed solid was filtered on filtering paper. Of the
15 filtered liquid, 25 mL was poured in a previously weighed aluminum container, which was heated in a stove of 140°C for at least 2 hours, under nitrogen flow and vacuum, to remove the solvent by evaporation. The container was then kept in an oven at 140°C under vacuum until constant weight was obtained. The weight percentage of polymer soluble in xylene at room temperature was then calculated.

20

Ethylene content

The ethylene content (C2 content) in the random propylene-ethylene copolymer was determined using ¹³C NMR according to known procedures.

25 Analytical temperature rising elution fractionation (aTREF)

Analytical temperature rising elution fractionation (aTREF) analysis was conducted according to the method described in U.S. Patent No. 4,798,081 and Wilde, L.; Ryle, T.R.; Knobloch, D. C; Peat, LR. ; Determination of Branching Distributions in Polyethylene and Ethylene Copolymers, J. Polym. ScL, 20, 441-455 (1982), which are
30 incorporated by reference herein in their entirety. The composition to be analyzed was dissolved in 1,2-dichlorobenzene of analytical quality filtrated via 0.2 µm filter and allowed to crystallize in a column containing an inert support (Column filled with 150 µm stainless steel beans (volume 2500µL) by slowly reducing the temperature to 30°C at a cooling rate of 0.1°C/min. The column was equipped with an infrared detector. An
35 ATREF chromatogram curve was then generated by eluting the crystallized polymer

sample from the column by slowly increasing the temperature of the eluting solvent (1,2-dichlorobenzene) from 30 to 140°C at a rate of 1°C/min.

The instrument used was Polymer Char Crystaf-TREF 300, with the following characteristics:

- 5 - Stabilizers: 1 g/L of a phenolic antioxidant (Topanol) + 1 g/L of a secondary antioxidant (Tris(2,4-di-tert-butylphenyl) phosphite, Irgafos 168 of BASF)
- Sample: approx. 40 mg in 20 mL
- Sample volume: 0.3 mL
- 10 - Pump flow: 0.50 mL/min

The software from the Polymer Char Crystaf-TREF-300 was used to generate the spectra.

CIELAB b-value

- 15 The CIELAB b-value (Colour value) is measured in the following manner. Colour measurements were done by using a Konica Minolta CM-5, measuring L*, a*, b* values (CIE), using a d8 geometry (measurements in reflectance), light source D65 and a 10° viewing angle with a 30 mm measurement opening. A white calibration tile is used as background. The colour measurement is done according to CIELAB (ASTM D6290-05) and ASTM E313. The b-values are disclosed in the Examples below.
- 20

- Investigated specimens were transparent plaques (62x62mm) with 3.2 mm thickness. These transparent plaques were subjected to gamma radiation. Chosen setting was gamma radiation with doses of 25 and 50 kGy. Irradiation was conducted at Synergy Health Ede B.V. in Etten-leur (The Netherlands). For gamma radiation which has a high penetration depth, the polymer was packaged in transparent bags without particular handling. Irradiation may take several hours. The gamma rays may result from the decay of the radioactive isotope Cobalt-60 (60Co). They have a high penetration depth and can penetrate complete pallets or lots.
- 25
- 30

Preparation of the catalyst

- Two different catalysts were prepared, Catalyst A, which was prepared using a phthalate containing internal electron donor, and Catalyst B, which was prepared using a phthalate-free internal electron donor. Catalyst A is a catalyst which was prepared according to Illustrative Embodiment 1 in US4728705A1, with the exception that di-
- 35

isobutyl-phthalate was used instead of ethyl benzoate. Catalyst B was synthesized according to Example 1 in EP0728724.

Polymerization process

5 A gas phase Unipol™ reactor was used to prepare the polymers. The conditions in the reactor were as follows: i) gas phase fluidized bed reactor had a superficial gas velocity around 30 m/s; ii) the polymerization reaction temperature was 64 to 70°C; the pressure was 29 bar with a corresponding partial pressure of propylene of 23 bar; iv) hydrogen was added for controlling the molar mass in a manner known per se. The residence time was 3 hours, and the throughput was 15 kg/hour. In the process di-
10 isopropyl dimethoxysilane (DiPDMS) was used as an external donor and triethylaluminium (TEAL) was used as a co-catalyst. The catalyst components are introduced in the polymerization stage. Furthermore, antistatic additives were used to prevent the particles from adhering to each other or to the walls of the reactor.

15

Polymerization conditions are indicated in Table 1 below. In this table, the following abbreviations are used:

- Al/Ti is the ratio of the co-catalyst (TEAL) to the procatalyst
- Si/Ti is the ratio of the external donor (DiPDMS) to the procatalyst
- 20 - Al/Si is the ratio of the co-catalyst (TEAL) to the external donor (DiPDMS)
- H₂/C₃ is the molar ratio of hydrogen to propylene.

Table 1

	Catalyst	P (bar)	T (°C)	Al/Ti (mol/mol)	Si/Ti (mol/mol)	Al/Si (mol/mol)	H ₂ /C ₃ (mol/mol)	C ₂ /C ₃ (mol/mol)
PP-01	A	30	64	50	16.5	~5.9 - 10	0.0658	0.0123
PP-02	B	31	64	55	18.3	3.0	0.0546	0.0203

PP-01 thus produced is phthalate containing random propylene-ethylene copolymer.

25 PP-02 is a phthalate-free random propylene ethylene copolymer.

PP-01 and PP-02 were characterized using the methods as described herein; results are shown in Table 2 below.

30 The aTREF spectra as recorded for PP-01 and PP-02 are shown in Figure 1 (Fig. 1). The x-axis shows the elution temperature (°C), the y-axis shows the signal. The peak (the highest point on the curve) was marked as 'peak T_m' and is noted for PP01 and PP02 in the below table.

The area under the aTREF curve was also determined and the area under the curve for a temperature $T = 110 - 1.66 * [C]$ equation 1 to a temperature of 120°C was listed in the below table. In addition, the total area under the curve for a temperature from 50 to 120°C was also listed.

- 5 In equation 1, T is the temperature in °C, wherein [C] is the comonomer content in the random propylene copolymer in wt%

10 The percentage of area under the aTREF curve at and above a temperature (T) to a temperature up to 120°C based on the total area under the aTREF curve in the temperature range from 50°C to 120°C was calculated by dividing the area under the curve for a temperature $\geq T$ (in °C) to 120°C by the total area under the curve from 50°C to 120°C and multiplication by 100.

Table 2

	MFR (dg/min)	XS (wt. %)	C2 content (wt. %)	Peak Tm (°C)	T	Area \geq T to 120°C	Area for 50 to 120°C	Area under aTREF curve (%)
PP-01	40		3.2	102.5	104.688	0.15328	1.51332	10.13
PP-02	40	6.4	3.1	100.2	104.854	0.0025	1.5399	0.16

15

Materials used

The following materials were used in the following examples.

PP-01 and PP-02 as obtained in the polymerization.

20

Additives

As phosphite compound (Phos.) was used tris(2,4-di-tert-butylphenyl)phosphite (Irgafos® 168 of BASF)

25

As hydroxylamine (HA) was used N,N-dioctadecylhydroxylamine (Irgastab® FS042 of BASF).

As clarifier additive (CA) was used 1,2,3-tridesoxy-4,6;5,7-bis-O-[(4-propylphenyl)methylene] nonitol sorbitol (Millad® NX8000 of Milliken).

As acid scavenger (AS) calcium stearate was used.

As phenolic antioxidant (PA) pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) is used (Irganox 1010 of BASF).

As hindered amine light stabilizer (HALS) butanedioic acid, dimethylester polymer with
 5 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol (Tinuvin® 622 of BASF) (HALS1) or
 poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-s-triazine-2,4-diy]] [2,2,6,6-tetramethyl-4-
 piperidinyl]imino]hexamethylene [(2,2,6,6-tetramethyl-4-piperidinyl) imino]]
 (Chimassorb®944 of BASF) (HALS-2) were used.

10 Preparation of polymer composition

Polymer compositions were prepared by blending (unstabilized) reactor polymer powder with the remaining components as disclosed in Table 3 during a compounding step. CE denote comparative examples and E denote examples according to the invention. CE1 is a comparative example containing a phthalate-containing
 15 polypropylene (PP01) and the following stabilizing additive mixture: a phenolic antioxidant (PA) in combination with a phosphite, a clarifying agent (CA) and a
 antistatic agent (AS). E1 is an example containing a phthalate-free polypropylene (PP02), and the following stabilizing additive mixture: a phenolic antioxidant (PA) in
 combination with a phosphite, a clarifying agent (CA) and an acid scavenger (AS). E2
 20 is an example containing a phthalate-free polypropylene (PP02), and the following stabilizing additive mixture: a phosphite, a hydroxyl amine (HA), a clarifying agent
 (CA), an acid scavenger (AS) and a hindered amine light stabilizer (HALS).

Table 3. Compositions of the examples. Each of the components is given in wt.%
 25 based on the weight of the polymer composition.

#	PP (type)	Phos.	HA	CA	AS	PA	HALS-1	HALS-2
CE1	99.595 (PP-01)	0.050	0.000	0.230	0.075	0.050	0.000	0.000
E1	99.595 (PP-02)	0.050	0.000	0.230	0.075	0.050	0.000	0.000
E2	99.495 (PP-02)	0.050	0.050	0.230	0.075	0.000	0.100	0.000
E3	99.495 (PP-01)	0.050	0.050	0.230	0.075	0.000	0.000	0.100
E4	99.495	0.050	0.050	0.230	0.075	0.000	0.100	0.000

(PP-01)								
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The irradiation resistance in terms of discolouration (yellowing) of the polymer compositions was tested by measuring the b-value as discussed above.

5 Table 4. yellowing (b-value) after irradiation

#	not irradiated	25kGy gamma	50kGy gamma
CE1	-3.01	10.63	13.99
E1	-2.33	1.35	2.84
E2	-3.45	-0.85	0.66

10 As can be derived from the results in Table 4, when using a composition comprising a random propylene-ethylene copolymer, wherein the polymer composition comprises less than 150ppm of phthalates based on the weight of the polymer composition (E1 and E2 using a phthalate-free random propylene-ethylene copolymer), a significantly improved non-yellowing is obtained as compared to using a composition that is phthalate-containing (CE1 using a phthalate-containing random propylene-ethylene copolymer).

15 In addition, it can be derived from the results in Table 4 that an even further reduction in yellowing can be achieved when the polymer composition comprising less than 150ppm of phthalates based on the polymer composition further comprises a stabilizing additive mixture, said stabilizing additive mixture comprising a hydroxylamine, a phosphite compound and a hindered amine light stabilizer (compare E1 to E2)

20

Table 5. yellowing (b-value) after irradiation

example	not irradiated	35kGy gamma	55kGy gamma	40kGy e-beam
E3	1.56	2.72	3.08	2.60
E4	1.55	2.24	2.68	2.15

25 In addition, it can be derived from the results in Table 5 for examples E3 and E4 that use of butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol (HALS-1) instead of poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-s-triazine-2,4-diy]] [2,2,6,6-tetramethyl-4-piperidiny]imino]hexamethylene [(2,2,6,6-tetramethyl-4-piperidiny) imino] (HALS-2) leads to less yellowing of the random

propylene-ethylene copolymer of the invention after irradiation (confirmed with 35kGy gamma, with 50kGy gamma or after irradiation with 40kGy e-beam).

CLAIMS

1. A healthcare article comprising a polymer composition comprising a random
5 propylene-ethylene copolymer, wherein the polymer composition comprises less than
150ppm, preferably less than 100ppm, more preferably less than 50 ppm, more
preferably less than 20ppm, most preferably 0 ppm of phthalates based on the weight
of the random propylene ethylene copolymer.
- 10 2. The article according to claim 1, wherein the random propylene-ethylene has a
melt flow rate in the range from 3.0 to 100 dg/min, preferably in the range from 6.0 to
90 dg/min, wherein the melt flow rate (MFR) is determined using ISO1133:2011
(2.16kg, 230°C) and/or wherein the random propylene-ethylene has an ethylene
content as determined using ¹³C NMR in the range from 0.5 to 6.0wt%, preferably in
15 the range from 1.5 to 4.5wt%, more preferably in the range from 2.0 to 4.0wt%, for
example in the range from 2.5 to 3.5 wt%.
3. The article according to claim 1 or claim 2, wherein the random propylene-
ethylene copolymer has a total amount of xylene solubles in the range from 1.0 to
20 8.0wt% as determined according to ISO16152:2005.
4. The article according to any one of the preceding claims, wherein the random
propylene-ethylene copolymer has a molecular weight distribution (Mw/Mn) in the
range from 3.0 to 10.0, for example in the range from 3.5 to 8.0, for example in the
25 range from 4.0 to 7.0, wherein Mw stands for the weight average molecular weight and
wherein Mn stands for the number average molecular weight and wherein Mw and Mn
are measured by SEC analysis with universal calibration according to ISO16016-
1(4):2003.
- 30 5. The article according to any one of the preceding claims, wherein the random
propylene-ethylene copolymer has an area under the aTREF curve at and above a
temperature (T) to a temperature up to 120°C of at most 5.0% based on the total area
under the aTREF curve in the temperature range from 50°C to 120°C
, wherein $T = 110 - 1.66*[C]$ equation 1
35 wherein T is the temperature in °C, wherein [C] is the comonomer content in the
random propylene copolymer in wt% , wherein the aTREF curve was generated using a

cooling rate of 0.1°C/min and a heating rate of 1°C/min and 1,2-dichlorobenzene as eluting solvent.

6. The article according to any one of the preceding claims, wherein the random
5 propylene-ethylene copolymer is present in the composition in an amount of at least
80wt% based on the weight of the polymer composition, for example at least 85wt%
based on the weight of the polymer composition, for example at least 90wt% based on
the weight of the polymer composition, for example at least 95wt% based on the weight
of the polymer composition, preferably at least 97wt% based on the weight of the
10 polymer composition, preferably at least 98wt% based on the weight of the polymer
composition, more preferably at least 99wt% based on the weight of the polymer
composition.

7. The article according to any one of the preceding claims, wherein the polymer
15 composition further comprises a stabilizing additive mixture, said stabilizing additive
mixture comprising a hydroxylamine, a phosphite compound and a hindered amine light
stabilizer, preferably, wherein said stabilizing additive mixture is present in an amount
from 0.040 to 0.60 wt.% based on the weight of the polymer composition, preferably
from 0.12 to 0.40 wt.%.
20

8. The article according to claim 7, wherein the hydroxylamine is N,N-
dioctadecylhydroxylamine and/or wherein the hydroxylamine present in an amount from
0.01 to 0.15 wt.% based on the weight of the polymer composition, preferably in an
amount from 0.03 to 0.10 wt.% based on the weight of the polymer composition.

9. The article according to claim 7 or claim 8, wherein the phosphite compound is
25 tris(2,4-di-tert-butylphenyl)phosphite and/or wherein the phosphite is present in an
amount from 0.01 to 0.15 wt.% based on the weight of the polymer composition,
preferably in an amount from 0.03 to 0.10 wt.%.

10. The article according to any one of claims 7-9, wherein the hindered amine
30 light stabilizer is butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-
tetramethyl-1-piperidine ethanol and/or wherein the hindered amine light stabilizer is
present in an amount from 0.02 to 0.30 wt.% based on the weight of the polymer
composition, preferably in an amount from 0.06 to 0.20 wt.% based on the weight of
35 the polymer composition.

11. The article according to any one of claims 7-10, wherein the polymer composition further comprises a clarifier additive, preferably wherein the clarifier additive is 1,2,3-tridesoxy-4,6;5,7-bis-O-[(4-propylphenyl) methylene] nonitol sorbitol.

5 12. The article according to any one of claims 7-11, wherein the polymer composition is free of phenolic additives, preferably wherein the polymer composition has less than 10 ppm of phenolic additives.

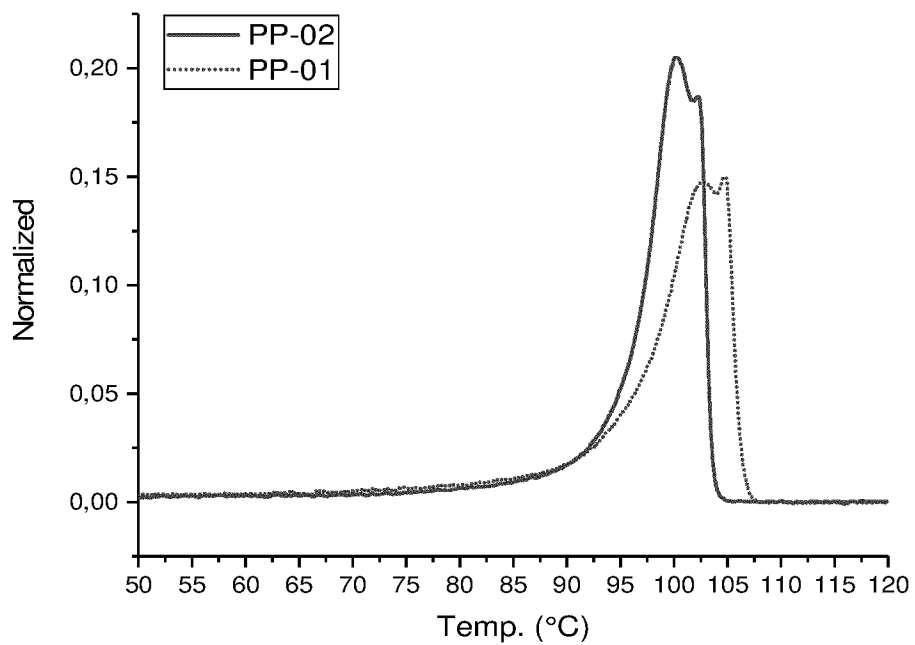
10 13. The article according to any one of the preceding claims, wherein said article has a CIELAB b-value, as determined according to ASTM D6290-05 and ASTM E313 of at most 4.0, preferably at most 3.0, more preferably of at most 2.5, even more preferably of at most 2.0 after having being subjected to at least 25 kGy gamma radiation, preferably after having been subjected to at least 50 kGy gamma radiation or at least 40 kGy electron beam radiation.

15

14. A polymer composition comprising a random propylene-ethylene copolymer and a stabilizing additive mixture, said stabilizing additive mixture comprising a hydroxylamine, a phosphite compound and a hindered amine light stabilizer, and optionally a clarifier additive, preferably wherein the polymer composition comprises 20 less than 150ppm, preferably less than 100ppm, more preferably less than 50 ppm, more preferably less than 20ppm, most preferably 0 ppm of phthalates based on the weight of the random propylene ethylene copolymer.

25 15. A use of the polymer composition of any one of claims 1-13 or according to claim 14 for manufacturing a healthcare article, for example wherein the healthcare article is a drug delivery article, laboratory ware, a medical device, a medical diagnostics article or healthcare packaging

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/074386

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08K5/32 C08K5/3435 C08K5/526 C08K5/12
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/086924 A1 (KING ROSWELL E [US]) 4 July 2002 (2002-07-04) Formulations G and H; paragraph [0132]; claims 1,4,5,18; tables 1-2	1-15
A	----- US 5 738 923 A (KO JOHN H [US] ET AL) 14 April 1998 (1998-04-14) column 6, lines 9-17 -----	1-15

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Date of the actual completion of the international search 5 November 2020	Date of mailing of the international search report 16/11/2020
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Lohner, Pierre
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2020/074386

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